UNITED STATES PATENT AND TRADEMARK OFFICE

I, John Neil Albert SWEENEY BSc, PhD, Dip. Trans. IoL, translator to RWS Group plc, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.

2. That I am well acquainted with the French and English languages.

3. That the attached is, to the best of my knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in France on 25 November 1998 under the number 98/14,930 and the official certificate attached hereto.

4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.

For and on behalf of RWS Group plc

The 18th day of December 2003

FRENCH REPUBLIC

INPI
INSTITUT NATIONAL DE LA PROPRIETE INDUSTRIELLE

PATENT

UTILITY CERTIFICATE – CERTIFICATE OF ADDITION

OFFICIAL COPY

The Director-General of the Institut National de la Propriété Industrielle certifies that the attached document is a true copy of an application for industrial property titleright filed at the Institute.

Drawn up in Paris, 26 NOV. 1999

On behalf of the Director-General of the
Institut National de la Propriété Industrielle
The Patent Department Head

[signature]

Martine PLANCHE

INPI

INSTITUT NATIONAL DE LA PROPRIETE INDUSTRIELLE

INSTITUT NATIONAL DE LA PROPRIETE INDUSTRIELLE

N° 55-1222

1

REQUEST

FOR GRANT OF AN INDUSTRIAL PROPERTY TITLE *

a	X	PATENT OF INVENTION
b		UTILITY CERTIFICATE
c		DIVISIONAL APPLICATION
d		CONVERSION OF A EUROPEAN PATENT APPLICATION

For c and d: specify number, nature and date of initial application

2 COMPULSORY OPTIONS at time of filing (except for utility certificates)

THE APPLICANT WISHES TO DEFER THE FORMULATION OF THE DOCUMENTATION REPORT: [ ] YES [X] NO

IF THE OPTION CHOSEN IS NO AND IF THE APPLICANT IS A PHYSICAL PERSON, HE REQUESTS THE GRADUATED PAYMENT OF THE FEE ON THE DOCUMENTATION REPORT: [ ] YES [X] NO

NATURE	NUMBER	DATE OF INITIAL APPLICATION

DATE DOCUMENTS FILED: 25.11.98

NATIONAL REGISTRATION N°: 98/14,930

DATE OF FILING: 25 NOV. 1998

3 NAME AND ADDRESS OF THE APPLICANT OR THE REPRESENTATIVE TO WHOM ALL CORRESPONDENCE SHOULD BE ADDRESSED

SOLVAY (Société Anonyme)
Direction Régionale pour la France
5, Rue François 1er,
F-75383 PARIS CEDEX 08 (FRANCE)

POSTAL CODE OF THE PLACE OF FILING: 99

4 NUMBER OF GENERAL POWER OF ATTORNEY:

5 REFERENCE OF THE CORRESPONDENT: Cas S 98/35

6 TELEPHONE NO. OF THE CORRESPONDENT:

7 TITLE OF INVENTION

Functional trifluorovinyl monomers and their copolymerization with fluoroolefins

8 APPLICANT: Name and forenames (underline the surname) or legal name and status

SOLVAY (Société Anonyme)

SIREN N°, WHERE APPLICABLE

9 COMPLETE ADDRESS

Rue du Prince Albert, 33
B-1050 BRUSSELS (BELGIUM)

COUNTRY: BELGIUM

10 NATIONALITY

Belgian

FEES PAID

- [X] FILING
- [X] DOCUMENTATION REPORT
- [ ] PRIORITY CLAIM
- [ ] EXCESS CLAIMS (from the 11th)

11 INVENTOR(S)

THE APPLICANT IS THE SOLE INVENTOR: [ ] YES [X] NO

(if the answer is no see explanatory note)

12 IF THE APPLICANT IS A PHYSICAL PERSON NOT REQUIRED TO PAY INCOME TAX HE REQUESTS* OR HAS REQUESTED A REDUCED RATE PAYMENT*: [ ] YES [X] NO

13 DECLARATION OF **PRIORITY** OR REQUEST FOR **BENEFIT OF FILING DATE** OF A PREVIOUS APPLICATION

COUNTRY OF ORIGIN	DATE OF FILING	NUMBER

14 [ ] DIVISIONS PREDATING THIS APPLICATION N° N° N° N°

15 SIGNATURE OF APPLICANT OR HIS REPRESENTATIVE NAME AND POSITION OF SIGNATORY REGISTRATION No.

SOLVAY (Société Anonyme)

(illegible signature)

SIGNATURE OF THE RECEIVING OFFICER

SIGNATURE AFTER REGISTRATION OF THE APPLICATION AT THE INPI

(illegible signature)

*Check as appropriate

SHADED BOXES ARE FOR OFFICIAL USE ONLY

INPI
INSTITUT
NATIONAL DE
LA PROPRIETE
INDUSTRIELLE

Cas S 98/35

PATENT, UTILITY CERTIFICATE

DESIGNATION OF THE INVENTOR
(if the applicant is not the inventor or the sole inventor)

PATENTS ADMINISTRATIVE DIVISION

26bis, rue de Saint-Petersbourg
75800 Paris Cédex 08
Tel: 01 53 04 53 04 - Fax: 01 42 93 59 30

NATIONAL REGISTRATION NO.

98/14,931

TITLE OF THE INVENTION:

Functional trifluorovinyl monomers and their copolymerization with fluoroolefins

THE UNDERSIGNED

SOLVAY (Société Anonyme)
Rue du Prince Albert, 33
B-1050 BRUSSELS (Belgium)

DESIGNATE(S) AS INVENTOR(S) (surname underlined, forenames, address):

1. PETROVA, Petya
   Quartier Dame Grouev,
   Bat. 8, Appart. 22
   SLIVEN
   BULGARIA

2. AMEDURI, Bruno
   Rue de la Treille Muscate, 28
   F-34090 MONTPELLIER
   FRANCE

3. KOSTOV, Georges
   Komplex Slaveykore,
   Bat. 38, Appart. 11
   8010 BOURGAS
   BULGARIA

4. BOUTEVIN, Bernard
   Rue Anselme Mathieu, 1
   F-34090 MONTPELLIER
   FRANCE

NOTE: In exceptional cases, the name of the inventor may be followed by that of the company to which he belongs (membership company) when the latter is other than the company which is the applicant or proprietor.

Date and signature(s) of the applicant(s) or of the representative

23 NOVEMBER 1998

(illegible signature)

Functional trifluorovinyl monomers and their copolymerization with fluoroolefins

The present invention relates to fluoromonomers. It also relates to processes for the copolymerization of fluoromonomers with fluoroolefins, to the resulting copolymers and to the use of these monomers in forming in particular fluoroelastomers. In addition, the present invention relates to a process for the crosslinking of these copolymers.

A large number of fluoromonomers have already been disclosed in the literature.

The synthesis of fluoroolefins corresponding to the general formula $CF_2=CF(CF_2)_m(CH_2)_nOH$ (with m = 0 to 10 and n = 1 to 4) is disclosed in Patent Application EP 0 138 091. The use of fluoroolefins as comonomers of vinylidene fluoride is also envisaged.

Patent Application EP 0 135 917 discloses fluorocopolymers formed by copolymerization of vinylidene fluoride with fluoroolefins of general formula $CF_2=CF(CF_2)_m(CH_2)_nX$ (with X = OH, COOH or an epoxide group, m = 0 to 10 and n = 1 to 4). The copolymerization of some of these compounds with vinylidene fluoride is described therein.

Patent US 3 483 263 discloses the synthesis of unsaturated haloalcohols corresponding to the formula $CX_1X_2=CX_3-A-OH$ in which X_1 to X_3 represent halogen atoms and A represents an alkylene group comprising at least two carbon atoms.

T. Nguyen et al., in J. Organic. Chem., 54(23), 5640-5642, 1989, disclose the synthesis of a compound corresponding to the formula $CF_2=CFCH_2OH$ by addition of methyllithium to 2,2,3,3-tetrafluoropropanol.

The document SU 375298 discloses the use of $CF_2=CFCH_2OH$ in the preparation of O-(2,3,3-trifluoroalkyl) phosphonates.

The document WO 86/07590 relates to pesticides corresponding to the general formula $CF_2=CF-(CH_2)_n-X-R$ in which X can be O, N, S or CH_2 and n can have the

values from 1 to 4, the value of R depending on the meaning of X.

The use of compounds of formula $CF_2{=}CF{-}CH_2Q$ as pesticides is revealed in United States of America Patent US 5 514 717.

W.R. Dolbier et al., in J. Chem. Soc. Perkin Trans., 2, 219-232, 1998, analysed the cyclization activities of hex-5-enyl radicals and disclosed, inter alia, the synthesis of the compound 4,5,5-trifluoropent-4-enol.

T. Dubuffet et al., in J. Organomet. Chem., 341, 11-18, 1998, reveal a process for the opening of oxetanes under the action of fluorinated organolithium derivatives. Test 13 gives access to the compound 4,5,5-trifluoropent-4-enol.

An object of the present invention consists in making available novel fluoromonomers.

This object is achieved by compounds corresponding to the formula I

$$CF_2{=}CF{-}(CH_2)_m{-}W \qquad (I)$$

in which

m has the value 1, 2 or 3,

W represents a $CH(OH)CH_2OH$ group, a $\underset{R_2}{\underset{|}{P}}{-}R_1$ group,

a $\overset{O}{\overset{\|}{\underset{R_4}{\underset{|}{P}}}}{-}R_3$ group, a $\overset{O}{\overset{\|}{\underset{R_6}{\underset{|}{P}}}}{-}OR_5$ group, a $\overset{O}{\overset{\|}{\underset{OR_8}{\underset{|}{P}}}}{-}OR_7$ group or a Y-Z group,

in which

R_1, R_2, R_3 and R_4 independently represent a hydrogen atom, a C_1-C_{20} alkyl group or an optionally substituted aryl group

R_5 and R_6 independently represent a hydrogen atom, a C_1-C_{20} alkyl group or an optionally substituted aryl group, with the proviso that, when R_5 represents a hydrogen atom, R_6 is other than a phenyl group when m has the value 1

R_7 and R_8 independently represent a hydrogen atom, a C_1-C_{20} alkyl group or an optionally substituted aryl group, with the proviso that R_7 and R_8 do not both represent a hydrogen atom or an ethyl group when m has the value 1

Y represents an oxygen atom or a sulphur atom and

Z represents a hydrogen atom, a CH_2CH_2OH group, a CH_2COOH group or a $COCH_3$ group,

with the proviso that, when W represents $CH(OH)CH_2OH$, m has the value 1, when Y represents an oxygen atom, Z is not a hydrogen atom and, when Y represents S, m has the value 3.

More particularly, the present invention provides compounds corresponding to the formula II

$$CF_2=CF-C_3H_6-Y-Z \qquad (II)$$

in which Y and Z are as defined above.

Another compound according to the present invention corresponds to the formula

$$CF_2=CF-CH_2-CH(OH)-CH_2OH.$$

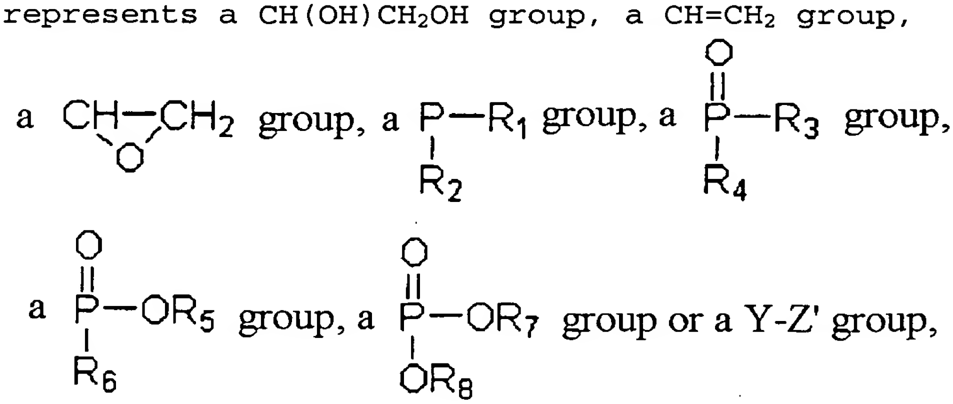
Another object of the present invention is a copolymerization process comprising the reaction of a compound corresponding to the formula I'

$$CF_2=CF-(CH_2)_m-W' \qquad (I')$$

in which

m has the value 1, 2 or 3,

W' represents a $CH(OH)CH_2OH$ group, a $CH=CH_2$ group,



in which

R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 independently represent a hydrogen atom, a C_1-C_{20} alkyl group or an optionally substituted aryl group

Y represents an oxygen atom or a sulphur atom and

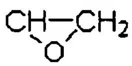
Z′ represents a hydrogen atom, a CH_2CH_2OH group, a CH_2COOH group or a $COCH_3$ group,

with a compound corresponding to the formula III

$$CF_2{=}CX_2 \qquad (III)$$

in which

X independently represents a hydrogen atom or a fluorine atom

with the proviso that, when m has the value 1 and X represents a hydrogen atom, W′ does not represent a  group,

so as to obtain a fluorocopolymer.

One embodiment of the present invention is a copolymerization process comprising the reaction of a compound corresponding to the formula I′

in which

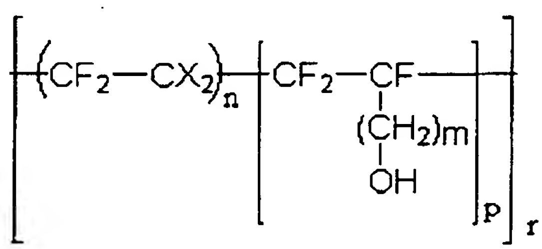
m has the value 1, 2 or 3,

W′ represents Y-Z′ and Y represents an oxygen atom and Z′ represents a hydrogen atom

with a compound corresponding to the formula III

in which X independently represents a hydrogen atom or a fluorine atom

so as to obtain a copolymer corresponding to the formula IV



(IV)

n, p and r independently representing natural integers.

An additional aspect of the present invention is a copolymerization process comprising the reaction of a compound corresponding to the formula I′

in which

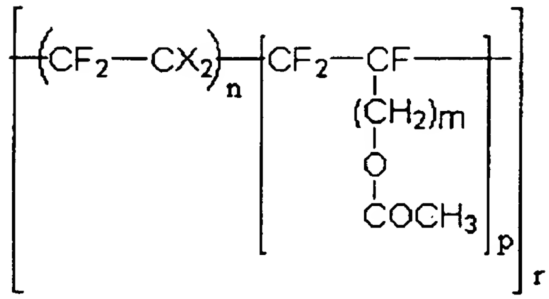
m has the value 1, 2 or 3,

W′ represents Y-Z′ and Y represents an oxygen atom and Z′ represents a $COCH_3$ group

with a compound corresponding to the formula III

in which X independently represents a hydrogen atom or a fluorine atom

so as to obtain a copolymer corresponding to the formula V



(V)

n, p and r independently representing natural integers.

The present invention also envisages a copolymerization process comprising the reaction of a compound corresponding to the formula I'

in which

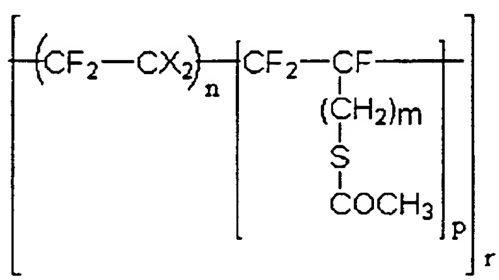
m has the value 1, 2 or 3,

W' represents Y-Z' and Y represents a sulphur atom and Z' represents a $COCH_3$ group

with a compound corresponding to the formula III

in which X independently represents a hydrogen atom or a fluorine atom

so as to obtain a copolymer corresponding to the formula VI



(VI)

n, p and r independently representing natural integers.

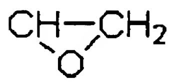
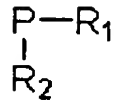
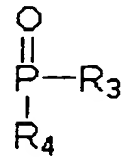
According to yet another preferred embodiment, a copolymerization process is provided comprising the reaction of a compound corresponding to the formula I'

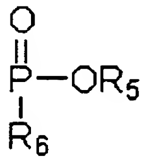
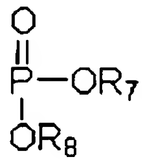
$$CF_2=CF-(CH_2)_m-W' \qquad (I')$$

in which

m has the value 1, 2 or 3,

W' represents a $CH(OH)CH_2OH$ group, a $CH=CH_2$ group,

a  group, a  group, a  group,

a  group, a  group or a Y-Z' group,

in which

R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 independently represent a hydrogen atom, a C_1-C_{20} alkyl group or an optionally substituted aryl group

Y represents an oxygen atom or a sulphur atom and

Z' represents a hydrogen atom, a CH_2CH_2OH group, a CH_2COOH group or a $COCH_3$ group,

with a compound corresponding to the formula III

$$CF_2{=}CX_2 \qquad (III)$$

in which

X independently represents a hydrogen atom or a fluorine atom

and with an olefinic compound so as to obtain a copolymer.

More particularly, the invention relates to a copolymerization process comprising the reaction of a compound corresponding to the formula I'

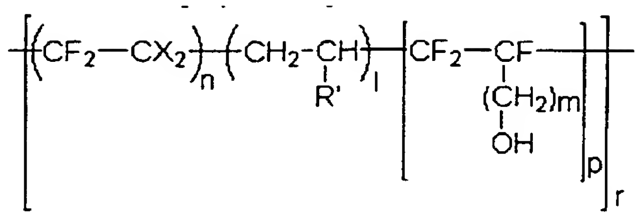
in which

m has the value 1, 2 or 3,

W' represents Y-Z' and Y represents an oxygen atom and Z' represents a hydrogen atom

with a compound corresponding to the formula III in which X independently represents a hydrogen atom or a fluorine atom

and with an olefinic compound of formula $CH_2{=}CHR'$ with R' representing a hydrogen atom or a C_1-C_4 alkyl group so as to obtain a copolymer corresponding to the formula VII

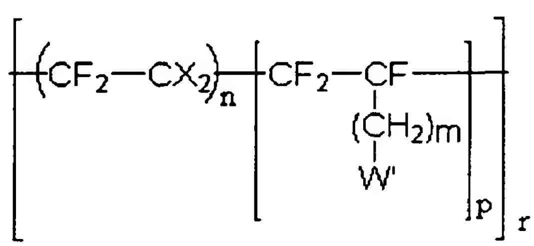


(VII)

l, n, p and r independently representing natural integers. Examples of C_1-C_4 alkyl groups are ethylene, propylene and butylenes [sic].

Fluoropolymers possess outstanding properties, such as their hydro- and oleophobicity, their thermal stability, their chemical inertia to acids, to bases, to solvents and to hydrocarbons, their resistance to ageing and to UV radiation and their low surface tension. They find highly varied applications, often in high-tech industries, such as microelectronics, the chemical industry, the automobile industry, the petroleum industry and the aeronautics industry. However, the high melting and glass transition temperatures of most of these polymers prove to be a limitation on their use which thus requires a significant energy input.

In order to limit this disadvantage, the present invention provides, according to another of its aspects, copolymers corresponding to the general formula VIII



(VIII)

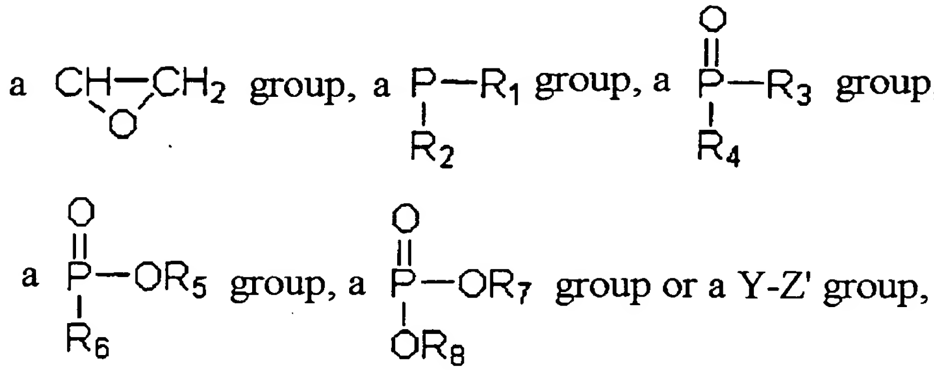
in which

m has the value 1, 2 or 3,

X independently represents a hydrogen atom or a fluorine atom,

n, p and r independently represent natural integers, and

W' represents a $CH(OH)CH_2OH$ group, a $CH=CH_2$ group,



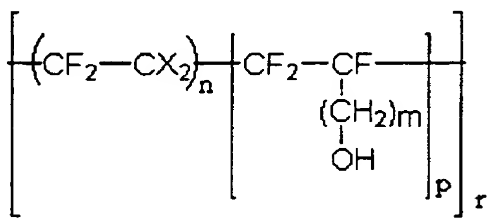
in which

R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 independently represent a hydrogen atom, a C_1-C_{20} alkyl group or an optionally substituted aryl group

Y represents an oxygen atom or a sulphur atom and

Z' represents a hydrogen atom, a CH_2CH_2OH group, a CH_2COOH group or a $COCH_3$ group.

More specifically, the present invention relates to copolymers corresponding to the formula IV



(IV)

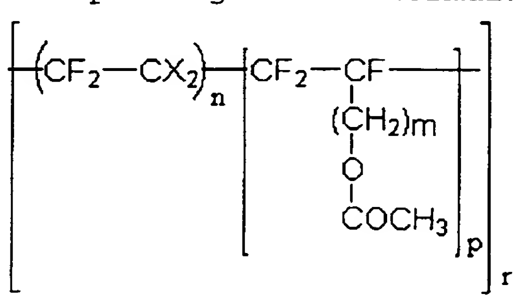
in which

m has the value 1, 2 or 3,

X independently represents a hydrogen atom or a fluorine atom and

n, p and r independently represent natural integers.

The present invention also relates to copolymers corresponding to the formula V



(V)

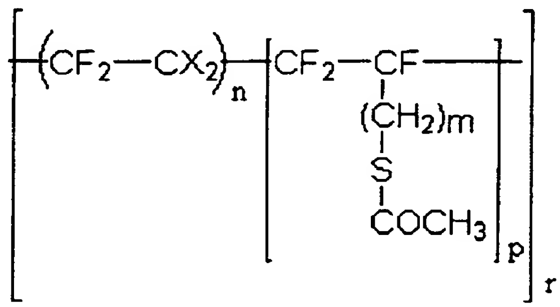
in which

m has the value 1, 2 or 3,

X independently represents a hydrogen atom or a fluorine atom and

n, p and r independently represent natural integers.

The present invention also relates to copolymers corresponding to the formula VI



(VI)

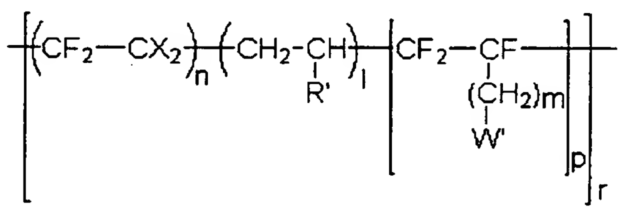
in which

m has the value 1, 2 or 3,

X independently represents a hydrogen atom or a fluorine atom and

n, p and r independently represent natural integers.

Other copolymers provided by the present invention are copolymers corresponding to the general formula IX



(IX)

in which

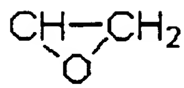
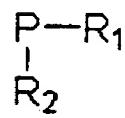
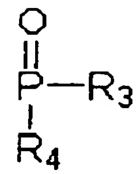
m has the value 1, 2 or 3,

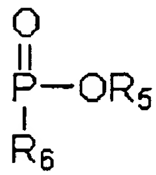
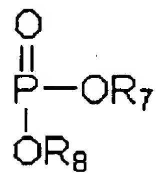
X independently represents a hydrogen atom or a fluorine atom,

l, n, p and r independently represent natural integers,

R' represents a hydrogen atom or a C_1-C_4 alkyl group and

W' represents a $CH(OH)CH_2OH$ group, a $CH=CH_2$ group,

a  group, a  group, a  group,

a  group, a  group or a Y-Z' group,

in which

R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 independently represent a hydrogen atom, a C_1-C_{20} alkyl group or an optionally substituted aryl group

Y represents an oxygen atom or a sulphur atom and

Z' represents a hydrogen atom, a CH_2CH_2OH group, a CH_2COOH group or a $COCH_3$ group.

More specifically, the present invention provides copolymers corresponding to the formula IX, in which

m has the value 1, 2 or 3,

X independently represents a hydrogen atom or a fluorine atom,

W' represents Y-Z' and Y represents an oxygen atom and Z' represents a hydrogen atom

l, n, p and r independently represent natural integers and R' represents a hydrogen atom or a C_1-C_4 alkyl group.

These copolymers comprise monomers exhibiting the CF_2=CF-R″-W' structure, R″ denoting a spacer arm of variable length targeted at introducing free volumes and at thus reducing the melting and glass transition temperatures.

In order to further improve the properties (particularly mechanical properties) of these fluoro(co)polymers, it is often desirable to crosslink them but this crosslinking to date has required the use of nucleophilic agents (such as diamines or bisphenols) or of radical systems (triallyl cyanurate radicals) or electron bombardment. Consequently, with the aim of

avoiding this additional stage, which constitutes a fairly complex procedure, the present invention provides for the incorporation of crosslinking sites (W' functional group in the above fluoromonomers) directly in the (co)polymers.

An additional object of the present invention is a crosslinking process comprising the stages of

a) optional deprotection of the functional groups of copolymers obtained above,

b) reaction of the resulting copolymers with an unconjugated C_5-C_8 diene,

so as to obtain crosslinked copolymers.

Examples of unconjugated dienes are 1,4-pentadiene, 1,5-hexadiene, 1,7-octadiene and 1,9-decadiene. The use of 1,5-hexadiene as unconjugated diene is particularly preferred.

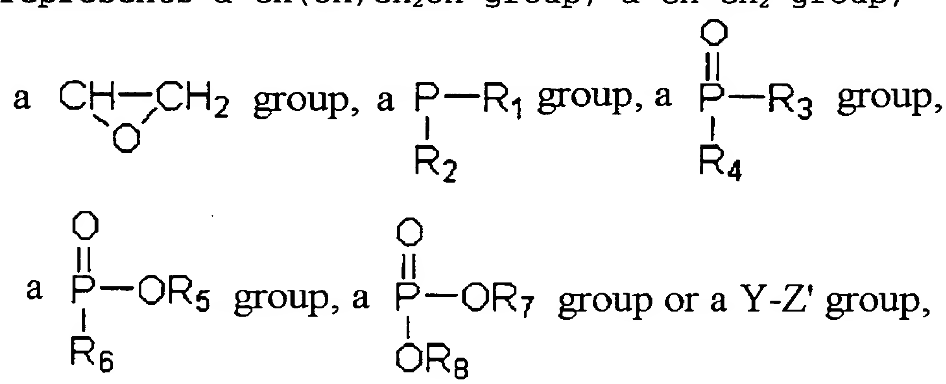
Finally, the use is also provided of compounds corresponding to the formula I'

$$CF_2{=}CF\text{-}(CH_2)_m\text{-}W' \qquad (I')$$

in which

m has the value 1, 2 or 3,

W' represents a $CH(OH)CH_2OH$ group, a $CH{=}CH_2$ group,



in which

R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 independently represent a hydrogen atom, a C_1-C_{20} alkyl group or an optionally substituted aryl group

Y represents an oxygen atom or a sulphur atom and

Z' represents a hydrogen atom, a CH_2CH_2OH group, a CH_2COOH group or a $COCH_3$ group,

with a compound corresponding to the formula III

$$CF_2=CX_2 \qquad (III)$$

in which X independently represents a hydrogen atom or a fluorine atom, preferably a hydrogen atom

and optionally with an olefinic compound, to form fluoroelastomers. Examples of olefinic compounds are ethylene, propylene and butylene. The olefinic compound is preferably propylene.

The invention is described in more detail, without implied limitation, in the following examples.

<u>Example 1</u>

Preparation of $CF_2=CFCH_2CH(OH)CH_2OH$

a) Radical addition of iododichlorotrifluoroethane to allyl acetate

A mixture composed of 292.2 g (1.050 mol) of iododichlorotrifluoroethane and of 106.5 g (1.065 mol) of allyl acetate was heated with stirring to 55°C in a three-necked round-bottomed flask equipped with a reflux condenser and a thermometer. 1.4 g (3.5 mmol) of t-butyl cyclohexyl peroxycarbonate were added at this temperature and, after 30 minutes, the addition of an equivalent amount of initiator results in an increase in the temperature of the reaction medium to 70°C. After 30 minutes, an additional 1.4 g of initiator were injected into the mixture and brought about a strong exothermic reaction to 175°C (over 10 seconds) which rendered the crude product colourless, followed by a dark brown mixture. After evaporating the unreacted iodo-dichlorotrifluoroethane and allyl acetate, the product mixture was distilled. Boiling point = 101-105°C/0.2 mmHg (lit. val.: 113°C/2 mmHg or 107-110°C/0.5 mmHg). 236.8 g (0.63 mol) of a dark liquid were obtained (yield = 60%).

b) Epoxidation

9.0 g (0.16 mol) of potassium hydroxide were introduced into 40 g of hexane in a three-necked round-bottomed flask equipped with a reflux

condenser and a mechanical stirrer. 30.5 g (0.08 mol) of the product resulting from the preceding stage were added dropwise to the mixture at ambient temperature. After completing the addition, the medium was heated to 70°C with stirring. After cooling, the KI precipitate was removed by filtration and the crude product was distilled. 11.95 g (0.057 mol) of a light brown liquid were obtained, boiling point = 53-55°C/23 mmHg (yield = 72%).

4,5-Dichloro-4,5,5-trifluoro-1,2-epoxypentane was produced in a proportion of 95.1%, whereas 5,5-dichloro-4,4,5-trifluoro-1,2-epoxypentane was obtained in a proportion of 4.9%.

c) Synthesis of halogenated 1,2-diol by opening of the epoxide ring

A mixture composed of 5.0 g (23.8 mmol) of 4,5-dichloro-4,5,5-trifluoro-1,2-epoxypentane, 11 ml of demineralized water, 11 ml of dioxane and 4 drops of 12N sulphuric acid was stirred in a single-necked round-bottomed flask equipped with a reflux condenser. The medium was heated at reflux for 12 hours. After the reaction, the dioxane was distilled off and the 4,5-dichloro-4,5,5-trifluoro-1,2-dihydroxypentane was extracted with diethyl ether, dried over sodium sulphate and distilled. Boiling point = 28-30°C/26 mmHg. 4.01 g (17.7 mmol) of a colourless liquid were obtained. Yield = 75% of 4,5-dichloro-4,5,5-trifluoro-1,2-dihydroxypentane.

d) Dechlorination of the 1,2-diol

A mixture of 2.37 g (0.036 mol) of activated zinc in 25 ml of dry DMF was stirred in a two-necked round-bottomed flask purged with argon and equipped with a reflux condenser. The temperature of the medium was increased to 70°C and 3.75 g (16.5 mmol) of 4,5-dichloro-4,5,5-trifluoro-1,2-dihydroxypentane obtained above were added dropwise. After reacting for 16 hours, the crude

product was cooled to ambient temperature and the unreacted zinc was removed by filtration. The filtrate was treated with 10% HCl and the product was extracted with 1,2,2-trifluorotrichloroethane. After distilling off the solvent, the $CF_2=CFCH_2CH(OH)CH_2OH$ was rectified in the form of a colourless liquid (0.88 g, 5.6 mmol, yield = 34%), boiling point = 106-110°C.

Example 2

Preparation of $CF_2=CFCH_2CH_2CH_2SCH_2COOH$

a) Photochemical initiation (excess of diene)

A Carius tube comprising 0.055 g (0.3 mmol) of benzophenone, 1.84 g (20 mmol) of thioglycolic acid, 5.00 g (41 mmol) of 1,1,2-trifluoro-1,4-pentadiene and 9.0 g of acetonitrile was cooled in an acetone/liquid nitrogen mixture and degassed under vacuum with 5 freezing/thawing cycles, so as to remove the oxygen. It was subsequently sealed and irradiated under a UV lamp for 16 hours. After the reaction, the tube was frozen in liquid nitrogen and opened, and the solvent and the volatile fractions were evaporated under vacuum (0.01 mmHg). 1,1,2-Trifluoro-6-thiaocten-8-oic acid was distilled first to give 1.9 g of a pale yellow liquid. Boiling point = 87-90°C/0.15 mmHg (yield = 44%).

b) Photochemical initiation (threefold excess of thioglycolic acid)

A similar test to that indicated above was carried out in the presence of 0.083 g (0.46 mmol) of benzophenone, 8.42 g (91.5 mmol) of thioglycolic acid, 3.72 g (30.5 mmol) of 1,1,2-trifluoro-1,4-pentadiene and 10.0 g of acetonitrile. After the same treatment and after the distillation of the excess thioglycolic acid, 5.29 g of a yellow wax were obtained (yield = 81%), 3,3,4-trifluoro-2,8-dithianonane-1,9-dioic [sic] acid.

c) Radical initiation in the presence of azobisisobutyronitrile (AIBN)

A stirred mixture composed of 0.049 g (0.3 mmol) of AIBN, 1.5 g (16.3 mmol) of thioglycolic acid, 1.99 g (16.3 mmol) of 1,1,2-trifluoro-1,4-pentadiene and 10 g of acetonitrile was heated at 80°C for 7 hours in a sealed Carius tube. After the reaction and the opening of the tube, the solvent and the unreacted starting materials were evaporated. The brown residue was eluted by flash chromatography on a silica bed with diethyl ether, so as to give an orange oil. The overall yield was 46%. In accordance with the integration of the characteristic signals of the ^1H and ^{19}F NMR spectra, the yields of 1,1,2-trifluoro-6-thiaocten-8-oic acid, of 3,3,4-trifluoro-2,8-dithianonane-1,9-dioic [sic] acid and of 4,5,5-trifluoro-6-thiaoctan-8-oic acid were 26, 37 and 37% respectively.

A similar experiment, initiated by t-butyl cyclohexyl peroxycarbonate, at 60°C for 5 hours gave 68% of 1,1,2-trifluoro-6-thiaocten-8-oic acid, 7% of 3,3,4-trifluoro-2,8-dithianonane-1,9-dioic [sic] acid and 25% of 4,5,5-trifluoro-6-thiaoctan-8-oic acid with an overall yield of 67%.

d) Radical initiation in the presence of di-t-butyl peroxide

Under similar conditions to those described above, 500 g (0.04 mol) of 1,1,2-trifluoro-1,4-pentadiene, 3.80 g (0.04 mol) of thioglycolic acid, 0.117 g (0.8 mmol) of di-t-butyl peroxide and 10 ml of acetonitrile were reacted. After stirring at 140°C for 6 h and after opening the tube, the solvent was evaporated and the residue was dried at 55°C under 0.1 mmHg to constant weight. A viscous brown liquid was obtained (4.3 g) which is insoluble in chloroform, acetone, DMF, dimethylacetaminde, THF and 1,2,2-trifluorotrichloroethane. The yield was 49% by mass.

Example 3

Preparation of $CF_2=CFCH_2CH_2CH_2SCH_2CH_2OH$

The reaction was carried out in a Carius tube comprising a stirred mixture composed of 0.19 g (1.0 mmol) of benzophenone, 2.70 g (34 mmol) of 2-mercaptoethanol, 5.01 g (41 mmol) of 1,1,2-trifluoro-1,4-pentadiene and 9.5 g of acetonitrile. After 6 freezing/thawing cycles, the tube was exposed to UV light at ambient temperature (approximately 25°C) for 14 hours. After a similar treatment, the crude product was purified and the $CF_2=CFCH_2CH_2CH_2SCH_2CH_2OH$ was distilled. 2.03 g of a colourless liquid were obtained (yield = 29%); boiling point 65-66°C/1 mmHg, 1,1,2-trifluoro-6-thiaoctanol.

Example 4

Preparation of $CF_2=CFCH_2OH$

12.4 g (94 mmol) of 2,2,3,3-tetrafluoropropanol, 62.5 ml (367 mmol) of anhydrous dibutyl ether and 9.5 g (94 mmol) of diisopropylamine were placed in a three-necked round-bottomed flask, dried under vacuum and purged with argon so as to remove moisture, equipped with a reflux condenser, a thermometer and a dropping funnel. The mixture was cooled to approximately 0°C. Subsequently, 100 ml (200 mmol) of a 2M solution of butyllithium in pentane were added dropwise for 30 minutes, so as to prevent the temperature from exceeding 5°C. After stirring for 1 hour, the medium was cooled to -50°C in an acetone/liquid nitrogen bath. The excess butyllithium was decomposed using a solution of concentrated sulphuric acid (9.4 ml in 30 ml of water) and the mixture was reheated to ambient temperature. The organic phase was separated by successive rinsings with a saturated sodium hydrogencarbonate solution and with water and then dried over anhydrous $MgSO_4$. Subsequently, the products were rectified at atmospheric pressure, so as to separate the pentane (boiling point 35°C), 32 mmol of 2,3,3-trifluoroallyl alcohol (boiling point 98°C) and the dibutyl ether

(134°C). Even after a second rectification, dibutyl ether was still present in the fluoroalcohol fraction and the yield obtained by ^{1}H and ^{19}F NMR was 34%.

Example 5

Preparation of $CF_2=CFC_3H_6OH$

a) Radical addition of 1-iodo-1,2-dichlorotrifluoroethane to allyl alcohol

1) Reaction at atmospheric pressure

A mixture composed of 171.1 g (0.617 mol) of $Cl(C_2F_3Cl)I$ and 98.3 g (1.69 mol) of allyl alchol was stirred in a three-necked round-bottomed flask equipped with a reflux condenser and a thermometer. The mixture was heated to 80°C and 2.30 g (0.014 mol) of AIBN were added thereto every hour. The reaction was monitored by gas phase chromatography (GC) until the iodinated reactant had been virtually completely consumed. Subsequently, the 2-iodo-4,5,5-trifluoro-4,5-dichloropentanol was distilled. 167.5 g (0.497 mol) of an orange-yellow liquid were obtained. Yield = 81%. Boiling point = 64-66°C/0.2 mmHg. 2-Iodo-4,5,5-trifluoro-4,5-dichloropentanol.

2) Reaction carried out in a Carius tube

A Carius tube saturated with nitrogen was filled with 40.0 g (0.14 mol) of $Cl(C_2F_3Cl)I$, with 17.1 g (0.28 mol) of allyl alcohol and with 0.92 g (0.014 mol) of copper powder. The tube was degassed by 5 freezing/thawing cycles and subsequently sealed. It was introduced into an oven incorporating agitation and heated at 120°C for 7 h. After the reaction and cooling to ambient temperature, the tube was frozen in liquid nitrogen and subsequently opened. Once ambient temperature was reached, the crude product was diluted in diethyl ether and the copper was removed by filtration. After an acid treatment, neutralization and evaporation of the solvent, the crude product was analysed by

GC. The yield was estimated at 62%, 2-iodo-4,5,5-trifluoro-4,5-dichloropentanol.

b) Reduction of 2-iodo-4,5,5-trifluoro-4,5-dichloropentanol

80.0 g (0.27 mol) of tributyltin hydride were added dropwise with stirring to 88.9 g (0.26 mol) of 2-iodo-4,5,5-trifluoro-4,5-dichloropentanol placed in a flask, saturated with argon and equipped with a septum, cooled in an ice bath. The addition took 30 minutes, the ice bath having been gradually reduced. The mixture was then stirred for an additional 3 hours at ambient temperature. Subsequently, the reduced derivative, 4,5-dichloro-4,5,5-trifluoropentanol, was distilled under reduced pressure. 47.2 g (0.225 mol) of a light yellow liquid were obtained (yield = 86.5%). Boiling point = 80-82°C/23 mmHg.

c) Dechlorination of 4,5-dichloro-4,5,5-trifluoropentanol

100 ml of dry DMF were introduced, via a septum, into a three-necked round-bottomed flask rinsed with a flow of argon and equipped with a reflux condenser. 46.8 g (0.72 mol) of zinc activated by 5 cm^3 of acetic acid and 5 cm^3 of acetic anhydride were introduced, with vigorous stirring, into the flask and the suspension was heated to 90°C. Subsequently, 50.0 g (0.237 mol) of 4,5-dichloro-4,5,5-trifluoropentanol were added dropwise and the temperature was maintained at 90°C for 4 hours after the completion of the addition. The reaction was monitored by GC, the respective retention times for the trifluorovinyl and chlorinated alcohols being 2.75 and 5.04 minutes respectively. After cooling, the excess zinc was removed by filtration and the crude product was treated with 10% HCl and the fluorinated fraction was extracted with diethyl ether. After distilling off the solvent, the 4,5,5-trifluoropent-4-en-1-ol was rectified. 23.3 g (0.166 mol) of a colourless

liquid were obtained. Boiling point = 53-55°C/24 mmHg (lit. val.: 95°C/155 mmHg). Yield = 70%.

Example 6

Preparation of $CF_2=CFCH_2CH_2CH_2OCOCH_3$

31.7 g (0.41 mol) of acetyl chloride were added dropwise to a two-necked round-bottomed flask, cooled in an ice bath, equipped with a reflux condenser (connected to a trap comprising potassium carbonate) and comprising 50.1 g (0.36 mol) of 4,5,5-trifluoropent-4-en-1-ol. The reactivity of the two reactants was monitored by sparging of HLC by the trap [sic]. After the completion of the addition, the reaction [sic] was stirred at ambient temperature until HCl was no longer being evolved (approximately 4 hours). After distillation, 59.3 g (0.326 mol) of 4,5,5-trifluoro-4-pentenyl acetate (colourless liquid) were obtained. Boiling point = 56-58°C/21 mmHg. (Yield = 91%),

Example 7

Copolymerization of trifluorovinyl alcohols with tetrafluoroethylene (TFE)

a) 2,3,3-Trifluoroallyl alcohol (FA1)

The copolymerization in solution (in 34% by weight of butyl ether) of TFE with 2,3,3-trifluoroallyl alcohol was carried out by a batchwise process in 30 and 50 cm^3 stainless steel autoclaves equipped with a magnetic stirrer, a safety valve, an accurate manometer (± 0.01 MPa) and a thermometer (± 0.2°C).

The autoclaves were charged with liquid monomer and initiator (AIBN), subsequently cooled with liquid nitrogen and purged several times by placing under a vacuum and by purging with nitrogen via a stainless [lacuna] pipe under a high vacuum. The technique of freezing/thawing cycles was used to remove oxygen from the liquid phase. Subsequently, the desired amount of TFE was condensed in the autoclave.

The polymerization reactions were carried out at various temperatures (60-75°C) under the pressure suitable for TFE to 10-12% conversion of the monomers.

After the polymerization, the unreacted TFE was purged and the comonomers were first recovered by distillation and subsequently the copolymer was dried under vacuum (10^{-2} mmHg at 50-60°C) to constant weight. The reactivity ratios r_i of the comonomers were calculated by the Tidwell and Mortimer methods and TFE proved to be more reactive than the monomer FA1 (r_{FA1} = 0.41 and r_{TFE} = 2.47).

b) 4,5,5-trifluoropent-4-en-1-ol (FA2)

The bulk copolymerization of TFE with 4,5,5-trifluoropent-4-en-1-ol was carried out by a batchwise process in 30 and 50 cm^3 stainless steel autoclaves equipped with a magnetic stirrer, a safety valve, an accurate manometer (± 0.01 MPa) and a thermometer (± 0.2°C).

The autoclaves were charged with liquid monomer and initiator (AIBN), subsequently cooled with liquid nitrogen and purged several times by placing under a vacuum and by purging with nitrogen via a stainless [lacuna] pipe under a high vacuum. The technique of freezing/thawing cycles was used to remove oxygen from the liquid phase. Subsequently, the desired amount of TFE was condensed in the autoclave.

The polymerization reactions were carried out at various temperatures (60-75°C) under the pressure suitable for TFE to 10-12% conversion of the monomers.

After the polymerization, the unreacted TFE was purged and the comonomers were first recovered by distillation and subsequently the copolymer was dried under vacuum (10^{-2} mmHg at 50-60°C) to constant weight. The reactivity ratios r_i of the comonomers were calculated by the Tidwell and

Mortimer methods and TFE proved to be more reactive than the monomer FA2 (r_{FA2} = 0.45 and r_{TFE} = 1.57).

Example 8

Emulsion (ternary) copolymerization of 4,5,5-trifluoropent-4-en-1-ol with tetrafluoroethylene (TFE) and propylene

A 250 cm^3 stainless steel autoclave (Buchi, Switzerland) was used as container for the terpolymerization of TFE with propylene and 4,5,5-trifluoropent-4-en-1-ol in a batchwise operation. The reactor was equipped with a cooling/heating jacket, with a paddle magnetic stirrer, with a pressure gauge, with a safety valve and with a measuring unit (monitoring of the pressure, stirring and temperature). The components were prepared separately (solutions A and B). The TFE/propylene monomer ratio was maintained at 80/20 mol% (total amount of monomers: 17.7 g) but the initial percentage of 4,5,5-trifluoropent-4-en-1-ol was varied within the range from 1.7 to 14.1 mol%.

The other components of all the compositions were as follows: H_2O (125 g); t-butanol[a] (36.8 g/l); $Na_2HPO_4 \cdot 12H_2O$[b]/NaOH[b] = 8/0.8 g/l; $C_7F_{15}COONH_4$(FC-143)[b] (10.10 g/l). The redox system comprised (mmol/l): t-butyl peroxobenzoate (TBPB)[a] (10.30); $FeSO_4 \cdot 7H_2O$[b] (0.22); EDTA·2Na2H_2O[b] [sic] (0.22); $HOCH_2SO_2Na \cdot 2H_2O$[b] (12.70), where "a" indicates the components of the solution A and "b" those of the solution B.

The autoclave was closed and the two solutions were purged by a flow of nitrogen. Subsequently, the reactor was charged with the two solutions under an inert atmosphere. The amounts of TFE and of propylene required in order to maintain their initial molar ratio at 80/20 and the initial pressure at 1.55 MPa for each experiment were introduced into the container while stirring at 800-850 rev/min. The temperature of the experiments was maintained by a thermostat at 25 ± 0.2°C. At the end of the copolymerization, the latex was coagulated by cooling the total product

mixture with liquid nitrogen and the copolymer isolated was dried under vacuum at 60°C to constant weight.

Example 9

Copolymerization of 4,5,5-trifluoro-4-pentenyl acetate (FAc) with vinylidene fluoride (VDF)

Bulk copolymerizations of vinylidene fluoride and of FAc were carried out in Carius tubes made of thick borosilicate in a batchwise process (length: 130 mm, internal diameter: 10 mm, thickness: 2.5 mm, for a total vol of 8 cm^3). After having introduced the initiator (0.05 mol% to the mixture of monomers) and the FAc, the tube was connected to a pipe for placing under vacuum and rinsed several times by placing under vacuum and by rinsing with helium. After 5 freezing/thawing cycles, the vinylidene fluoride was trapped under vacuum in the tube frozen with liquid nitrogen, after the reduction in pressure in a calibrated pressure intermediate metal container. The required amount of vinylidene fluoride (0.50-1.00 g) introduced into the tube was obtained by a relative fall in the pressure in this pressure-reducing container fed initially via a 300 g cylinder of vinylidene fluoride.

The tube, under vacuum and immersed in liquid nitrogen, was sealed and placed in the chamber of an oven incorporating agitation at 120°C for 17 hours.

After the copolymerization, the tube was frozen in liquid nitrogen and subsequently opened and the total product mixture was dried at 80°C under 10^{-2} mmHg to constant weight.

The composition of the copolymer (that is to say the content of vinylidene fluoride and of FAc in the copolymer) was determined by NMR spectroscopy at ambient temperature. The ^1H and ^{19}F NMR spectra were recorded on Bruker AC-200 or Bruker AC-250 instruments using deuterated acetone or dimethylformamide as solvents and tetramethylsilane (TMS) or $CFCl_3$ as internal references, respectively.

The radical copolymerization of the vinylidene fluoride (VDF) with 4,5,5-trifluoro-4-pentenyl acetate (FAc) was studied over a broad range of initial monomer compositions. ^{1}H NMR spectroscopy and ^{19}F NMR spectroscopy made it possible to determine the compositions of copolymers and the two results obtained were in good agreement. The reactivity ratios r_i of the comonomers were calculated by the Tidwell and Mortimer methods and the FAc monomer proved to be more reactive than vinylidene fluoride (r_{VDF} = 0.17 and r_{FAc} = 3.22). These values show that a random copolymerization took place. By taking into account the Q and e values of VDF, the Q and e parameters of FAc were calculated: e_{FAc} = 1.14-1.23 (from e_{VDF} = 0.40-0.50) and Q_{FAc} = 0.04-0.06 (in contrast to Q_{VDF} = 0.008-0.015).

Example 10

Copolymerization of 1-thio-4,5,5-trifluoro-4-pentenyl acetate (FSAc) with vinylidene fluoride (VDF)

A 200 ml Hastelloy autoclave, equipped with a valve, a manometer and a safety disc and provided with a magnetic stirrer, was charged with 0.2507 g (1.72 mmol) of t-butyl peroxide, with 4.01 g (0.0202 mol) of FSAc and with 70 g of acetonitrile. After being closed, the autoclave was placed in a bath of liquid nitrogen/acetone; subsequently, it was placed under vacuum and purged with gaseous nitrogen, so as to remove the oxygen. 20.25 g (0.316 mol) of vinylidene fluoride were then introduced. After reheating to ambient temperature, the autoclave was introduced into an oil bath with the following heating cycle: 5 h at 120°C, 2 h at 130°C and subsequently 6 h at 140°C. After the reaction, the container was placed in an ice bath and the unreacted vinylidene fluoride was released.

A portion of the acetone of the reaction mixture was evaporated and the vinylidene fluoride/FSAc copolymer was precipitated from a threefold excess of

heptane. The solid polymer was dried at 60-70°C under vacuum to constant weight.

4.36 g of a white solid were obtained (yield of approximately 18%).

This powder was soluble in acetone, acetonitrile, DMF and THF at ambient temperature but it was insoluble in cyclohexane, hexane, heptane and toluene, even on heating slightly (40°C).

Example 11

Crosslinking of poly(vinylidene fluoride) (PVDF) carrying mercapto functional side groups

a) Hydrolysis of the VDF/FSAc copolymer

10 ml of methanol and 10 ml of acetone were introduced into a three-necked round-bottomed flask equipped with a reflux condenser and an inlet for a flow of nitrogen. After degassing and after sparging nitrogen with this mixture [sic], 0.18 g (2.77 mmol) of potassium cyanide and 3.2 g (approximately 1.28 mmol) of VDF/FSAc copolymer were added.

The mixture was stirred at ambient temperature for 15 h. After the reaction, the hydrolysed copolymer was precipitated from water. 1.79 g of PVDF carrying mercapto functional side groups were obtained.

b) Crosslinking proper

A small tube made of borosilicate comprising 1.13 g (0.45 mmol) of PVDF carrying mercapto functional side groups, 1.30 g (15.8 mmol) of 1,5-hexadiene, 0.055 g (0.31 mmol) of t-butyl peroxypivalate and 5.04 g of acetonitrile were [sic] degassed and purged with helium. Subsequently, after 5 freezing/thawing cycles, it was sealed under vacuum and introduced into an oven with stirring. The tube was stirred for 5 h at 75°C. After the reaction, a beige precipitate appeared at the bottom of the tube. After freezing in liquid nitrogen, the tube was opened. The solvent and the excess 1,5-hexadiene were

evaporated and the brown solid was dried at 70°C under vacuum for 3 h (1.43 g were obtained). The product was insoluble in polar and nonpolar solvents.

CLAIMS

1. Compound corresponding to the formula I

$$CF_2=CF-(CH_2)_m-W \qquad (I)$$

in which

m has the value 1, 2 or 3,

W represents a $CH(OH)CH_2OH$ group, a $\underset{\displaystyle R_2}{\underset{|}{P}}-R_1$ group, a $\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle R_4}{\underset{|}{P}}}}-R_3$ group, a $\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle R_6}{\underset{|}{P}}}}-OR_5$ group, a $\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle OR_8}{\underset{|}{P}}}}-OR_7$ group or a Y-Z group,

in which

R_1, R_2, R_3 and R_4 independently represent a hydrogen atom, a C_1-C_{20} alkyl group or an optionally substituted aryl group

R_5 and R_6 independently represent a hydrogen atom, a C_1-C_{20} alkyl group or an optionally substituted aryl group, with the proviso that, when R_5 represents a hydrogen atom, R_6 is other than a phenyl group when m has the value 1

R_7 and R_8 independently represent a hydrogen atom, a C_1-C_{20} alkyl group or an optionally substituted aryl group, with the proviso that R_7 and R_8 do not both represent a hydrogen atom or an ethyl group when m has the value 1

Y represents an oxygen atom or a sulphur atom and

Z represents a hydrogen atom, a CH_2CH_2OH group, a CH_2COOH group or a $COCH_3$ group,

with the proviso that, when W represents $CH(OH)CH_2OH$, m has the value 1, when Y represents an oxygen atom, Z is not a hydrogen atom and, when Y represents S, m has the value 3.

2. Compound according to Claim 1, corresponding to the formula II

$$CF_2=CF-C_3H_6-Y-Z \qquad (II)$$

in which Y and Z are as defined in Claim 1.

3. Compound according to Claim 1, corresponding to the formula

$CF_2=CF-CH_2-CH(OH)-CH_2OH$.

4. Copolymerization process comprising the reaction of a compound corresponding to the formula I'

$$CF_2=CF-(CH_2)_m-W' \qquad (I')$$

in which

m has the value 1, 2 or 3,

W' represents a $CH(OH)CH_2OH$ group, a $CH=CH_2$ group,

a $\underset{\diagdown O \diagup}{CH-CH_2}$ group, a $\underset{R_2}{\underset{|}{P}}-R_1$ group, a $\overset{O}{\overset{\|}{\underset{R_4}{\underset{|}{P}}}}-R_3$ group,

a $\overset{O}{\overset{\|}{\underset{R_6}{\underset{|}{P}}}}-OR_5$ group, a $\overset{O}{\overset{\|}{\underset{OR_8}{\underset{|}{P}}}}-OR_7$ group or a Y-Z' group,

in which

R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 independently represent a hydrogen atom, a C_1-C_{20} alkyl group or an optionally substituted aryl group

Y represents an oxygen atom or a sulphur atom and

Z' represents a hydrogen atom, a CH_2CH_2OH group, a CH_2COOH group or a $COCH_3$ group,

with a compound corresponding to the formula III

$$CF_2=CX_2 \qquad (III)$$

in which

X independently represents a hydrogen atom or a fluorine atom

with the proviso that, when m has the value 1 and X represents a hydrogen atom, W' does not represent a $\underset{\diagdown O \diagup}{CH-CH_2}$ group,

so as to obtain a fluorocopolymer.

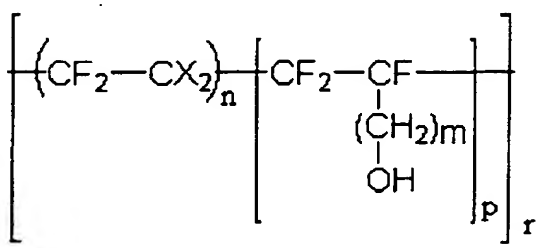
5. Copolymerization process according to Claim 4, comprising the reaction of a compound corresponding to the formula I'

in which

m has the value 1, 2 or 3,

W' represents Y-Z' and Y represents an oxygen atom and Z' represents a hydrogen atom

with a compound corresponding to the formula III in which X independently represents a hydrogen atom or a fluorine atom so as to obtain a copolymer corresponding to the formula IV



(IV)

n, p and r independently representing natural integers.

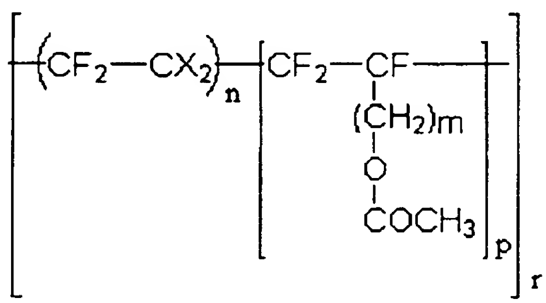
6. Copolymerization process according to Claim 4, comprising the reaction of a compound corresponding to the formula I'

in which

m has the value 1, 2 or 3,

W' represents Y-Z' and Y represents an oxygen atom and Z' represents a $COCH_3$ group

with a compound corresponding to the formula III in which X independently represents a hydrogen atom or a fluorine atom so as to obtain a copolymer corresponding to the formula V



(V)

n, p and r independently representing natural integers.

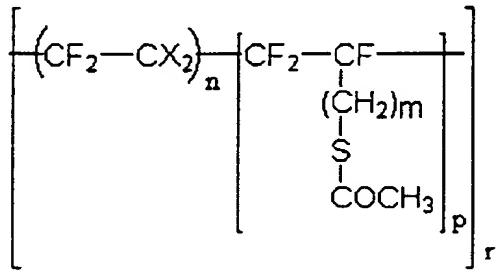
7. Copolymerization process according to Claim 4, comprising the reaction of a compound corresponding to the formula I'

in which

m has the value 1, 2 or 3,

W' represents Y-Z' and Y represents a sulphur atom and Z' represents a $COCH_3$ group

with a compound corresponding to the formula III in which X independently represents a hydrogen atom or a fluorine atom so as to obtain a copolymer corresponding to the formula VI



(VI)

n, p and r independently representing natural integers.

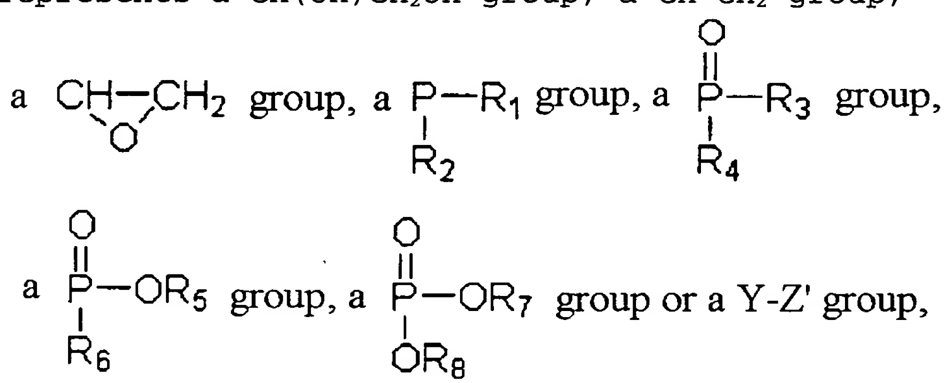
8. Copolymerization process comprising the reaction of a compound corresponding to the formula I'

$$CF_2{=}CF{-}(CH_2)_m{-}W' \qquad (I')$$

in which

m has the value 1, 2 or 3,

W' represents a $CH(OH)CH_2OH$ group, a $CH{=}CH_2$ group,



in which

R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 independently represent a hydrogen atom, a C_1-C_{20} alkyl group or an optionally substituted aryl group

Y represents an oxygen atom or a sulphur atom and

Z' represents a hydrogen atom, a CH_2CH_2OH group, a CH_2COOH group or a $COCH_3$ group,

with a compound corresponding to the formula III

$$CF_2{=}CX_2 \qquad (III)$$

in which

X independently represents a hydrogen atom or a fluorine atom

and with an olefinic compound so as to obtain a copolymer.

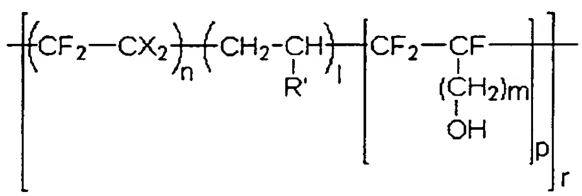
9. Copolymerization process according to Claim 8, comprising the reaction of a compound corresponding to the formula I'

in which

m has the value 1, 2 or 3,

W' represents Y-Z' and Y represents an oxygen atom and Z' represents a hydrogen atom

with a compound corresponding to the formula III in which X independently represents a hydrogen atom or a fluorine atom and with an olefinic compound of formula $CH_2=CH-R'$ in which R' represents a hydrogen atom or a C_1-C_4 alkyl group so as to obtain a copolymer corresponding to the formula VII



(VII)

l, n, p and r independently representing natural integers.

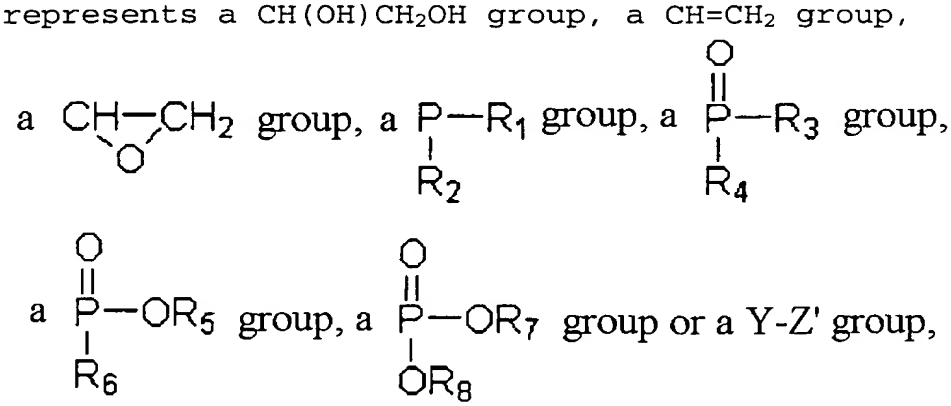
10. Use of compounds corresponding to the formula I'

$$CF_2=CF-(CH_2)_m-W' \qquad (I')$$

in which

m has the value 1, 2 or 3,

W' represents a $CH(OH)CH_2OH$ group, a $CH=CH_2$ group,



in which

R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 independently represent a hydrogen atom, a C_1-C_{20} alkyl group or an optionally substituted aryl group

Y represents an oxygen atom or a sulphur atom and

Z' represents a hydrogen atom, a CH_2CH_2OH group, a CH_2COOH group or a $COCH_3$ group,

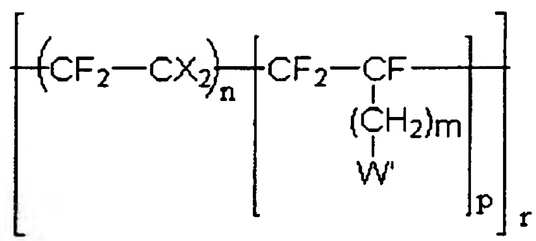
with a compound corresponding to the formula III

$$CF_2=CX_2 \qquad (III)$$

in which X independently represents a hydrogen atom or a fluorine atom, preferably a hydrogen atom and optionally with an olefinic compound, to form fluoroelastomers.

11. Use according to Claim 10, in which the olefinic compound is propylene.

12. Copolymer corresponding to the general formula VIII



(VIII)

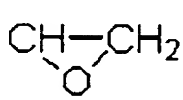
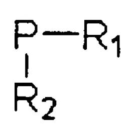
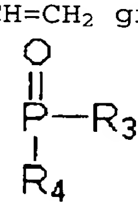
in which

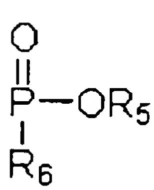
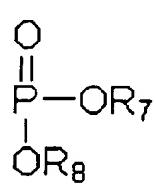
m has the value 1, 2 or 3,

X independently represents a hydrogen atom or a fluorine atom,

n, p and r independently represent natural integers, and

W' represents a $CH(OH)CH_2OH$ group, a $CH=CH_2$ group,

a  group, a  group, a  group,

a  group, a  group or a Y-Z' group,

in which

R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 independently represent a hydrogen atom, a C_1-C_{20} alkyl group or an optionally substituted aryl group

Y represents an oxygen atom or a sulphur atom and

Z′ represents a hydrogen atom, a CH_2CH_2OH group, a CH_2COOH group or a $COCH_3$ group.

13. Copolymer according to Claim 12, in which

m has the value 1, 2 or 3,

X independently represents a hydrogen atom or a fluorine atom, and

W′ represents a Y-Z′ group,

in which

Y represents an oxygen atom and

Z′ represents a hydrogen atom.

14. Copolymer according to Claim 12, in which

m has the value 1, 2 or 3,

X independently represents a hydrogen atom or a fluorine atom, and

W′ represents a Y-Z′ group,

in which

Y represents an oxygen atom and

Z′ represents a $COCH_3$ group.

15. Copolymer according to Claim 12, in which

m has the value 1, 2 or 3,

X independently represents a hydrogen atom or a fluorine atom, and

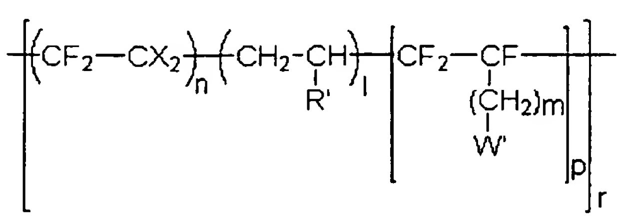
W′ represents a Y-Z′ group,

in which

Y represents a sulphur atom and

Z′ represents a $COCH_3$ group.

16. Copolymer corresponding to the general formula IX



(IX)

in which

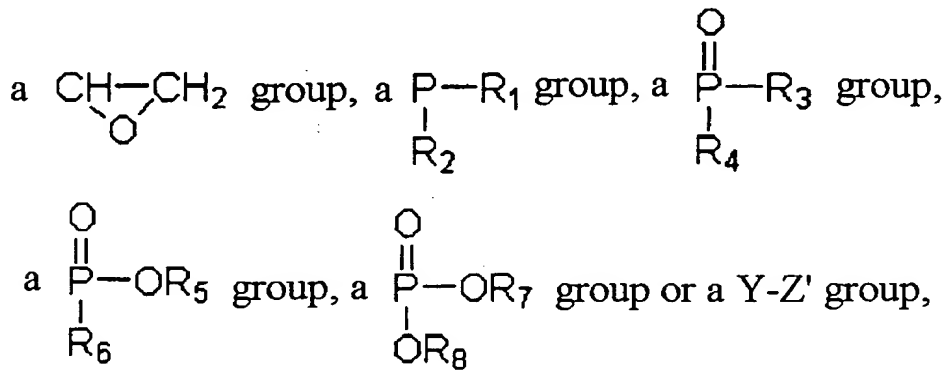
m has the value 1, 2 or 3,

X independently represents a hydrogen atom or a fluorine atom,

l, n, p and r independently represent natural integers,

R' represents a hydrogen atom or a C_1-C_4 alkyl group and

W' represents a $CH(OH)CH_2OH$ group, a $CH=CH_2$ group,



in which

R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 independently represent a hydrogen atom, a C_1-C_{20} alkyl group or an optionally substituted aryl group

Y represents an oxygen atom or a sulphur atom and

Z' represents a hydrogen atom, a CH_2CH_2OH group, a CH_2COOH group or a $COCH_3$ group.

17. Copolymer according to Claim 16, in which

m has the value 1, 2 or 3,

X independently represents a hydrogen atom or a fluorine atom,

W' represents Y-Z' and Y represents an oxygen atom and Z' represents a hydrogen atom

l, n, p and r independently represent natural integers and R' represents a hydrogen atom or a C_1-C_4 alkyl group.

18. Crosslinking process comprising the stages of

a) optional deprotection of the functional groups of copolymers according to one or more of Claims 12 to 17,

b) reaction of the resulting copolymers with an unconjugated C_5-C_8 diene,

so as to obtaine crosslinked copolymers.

19. Process according to Claim 18, in which the unconjugated diene is 1,5-hexadiene.